Influence of Light Curing Time and Overlying Ceramic Thickness on Polymerization Kinetics of Conventional and Self-adhesive Dual-cure Resin Cements

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감사의 글

먼저 이 논문을 완성하기까지 모든 과정을 세심하게 지도해 주시고 항상 따뜻한 관심으로 지원해주시는 노병덕 교수님께 진심으로 감사 드립니다. 또한 실험 및 논문 작성, 그리고 논문 심사의 전 과정 동안 좋은 논문을 작성할 수 있도록 꼼꼼한 지적과 아낌없는 격려의 말씀을 주신 박성호 교수님, 박정원 교수님, 김광만 교수님, 김예미 교수님께도 깊은 감사의 말씀을 드립니다. 많이 부족했던 제가 수련 과정 동안 여러 면에서 성장할 수 있도록 지도해 주신 주신 이찬영 교수님, 이승종 교수님, 김의성 교수님, 정일영 교수님, 신수정 교수님, 신유석 교수님께도 항상 감사 드립니다. 앞으로 어디에 있든지 선생님들의 가르침을 잊지 않고 자랑스런 보존과의 일원으로서 제 책무를 다할 수 있도록 노력하겠습니다. 더불어 저의 전공의 생활을 따뜻한 기억으로 채워준 성주, 재만이, 희준이, 자현이 그리고 선배님들과 후배님들에게도 감사한 마음을 전합니다. 마지막으로 제가 지금의 자리에 있기까지 사랑과 기도로 키워주시고 물심 양면으로 지원해주시는, 사랑하는 어머니, 아버지, 그리고 외할머니와 영찬이에게 그간 못다한 감사와 사랑을 전합니다.

2015년 12월

장 영 준

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Influence of Light Curing Time and Overlying Ceramic Thickness on Polymerization Kinetics of Conventional and Self-adhesive Dual-cure Resin Cements

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The purpose of this study was to investigate the influence of light curing time and overlying ceramic thickness on the polymerization of conventional and self-adhesive dual-cure resin cements.

Two conventional dual-cure resin cements (Rely-X ARC, Duolink) and two self-adhesive dual-cure resin cements (Rely-X U200, Maxcem Elite) were polymerized under different curing modes (dual-cure or self-cure), curing times (20 and 120 seconds), and different thickness of a ceramic overlay (2 and 4 mm). Polymerization kinetics was measured by FTIR for the initial 10

minutes and after 24 hours. Data were analyzed using one-way ANOVA/Student-Newman-Keuls post hoc test, and paired t-test (α=0.05).

When light curing time was set to 20 seconds, the presence of the ceramic block significantly affected degree of conversion (DC) of all resin cements ($p<0.05$). Especially, the DC of the 4 mm-20 sec group was significantly lower than that of the self-cured groups at 24 hours after polymerization ($p<0.05$). However when light curing time was set to 120 seconds, a similar DC compared to the positive control group ($p>0.05$) was achieved in all dual-cure groups except Maxcem Elite, at 24 hours after polymerization. Curing modes (dual-cure or self-cure), curing times (20 and 120 seconds), and ceramic overlay thickness (2 and 4 mm) significantly affected the DC of conventional and self-adhesive dual-cure resin cements.

When a ceramic restoration thickness is 4 mm or greater, 20 seconds of light curing time could result in a poor extent of polymerization, even lower than that of self-curing alone. Prolonging light curing time (120 seconds) could be an option to improve polymerization of conventional and self-adhesive dual-cure resin cements.

Keywords: Ceramics, Curing time, Degree of conversion, Polymerization kinetics, Resin cement

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I. Introduction

Dual-cure resin cements rely both on light-cure and chemical-cure mechanisms, in an attempt to ensure sufficient polymerization throughout the material, even without proper light activation. However, it has been shown that even dual-cure resin cements cannot reach as high a level of polymerization as expected when they are not properly light-activated due to light attenuation from the overlying indirect restoration (Arrais et al., 2008; Lee and Um, 2001;

Meng et al., 2006; Ozyesil et al., 2004). Oliveira et al. (Oliveira et al., 2012) observed significantly lower degree of conversion (DC) of dual-cured resin cement, compared to the self-cured group, when the former was light-cured for only 20 seconds under a 3 mm-thick ceramic disk. Meng et al. (Meng et al., 2008) also reported poor microhardness of dual-cure resin cements, even lower than the self-cured group, when it was insufficiently light-activated through a 3 mm-thick ceramic restoration overlay. These results point out that insufficient light activation is a factor that compromises the polymerization of dual-cure resin cements.

In this regard, it seems that manufacturers are not properly considering ceramic thickness when recommending light curing time for dual-cure resin cements. Moreover, several are recommending even further reduced light curing times for some products, including self-adhesive dual-cure resin cements, i.e. 20 seconds or below, even in the presence of a ceramic restoration. In addition, though many researchers have suggested increasing the light curing time to improve polymerization of dual-cure resin cements, there is minimal research verifying the clinical efficacy of prolonged light curing time through overlying ceramic restorations (Archegas et al., 2012). Therefore, there is a need to examine the influence of insufficient light activation on polymerization of dual-cure resin cements, including self-

adhesive dual-cure resin cements, when cured through a thick ceramic overlay or with a short light curing time.

The purpose of this study was to investigate the influence of light curing time and overlying ceramic thickness on the polymerization of conventional and self-adhesive dual-cure resin cements. The null hypotheses tested were that:

(i) The curing modes, i.e. dual-cure or self-cure mode, would not change the degree of conversion of dual-cured cements.

(ii) An overlay ceramic restoration of thickness 2 and 4 mm would not affect the degree of conversion of the dual-cured cements.

(iii) Curing times of 20 and 120 seconds would not affect the degree of conversion of dual-cured cements.

II. Materials and methods

1. FABRICATION OF CERAMIC BLOCKS

Lithium disilicate ceramic blocks (IPS e.max CAD/CAM, shade A3, low translucency, Ivoclar Vivadent, Schaan, Liechtenstein) were cut by low-speed diamond saw (Dk-2610, Struers Minitom, Rodovre, Denmark) in 10 mm x 10 mm size and polished with 400, 600 and 800-grit silicon carbide papers, and their final thickness were adjusted to 2.00±0.01 and 4.00±0.01 mm. They were cleaned with ultrasonic cleaner (BioSonic UC50D, Coltène/Whaledent, OH, USA) for 5 minutes, and then subjected to the crystallization process in a ceramic furnace (Programat P300, P81 mode, Ivoclar Vivadent, Schaan, Liechtenstein).

2. EXPERIMENTAL GROUPS

Two conventional dual-cure resin cements and two self-adhesive dual-cure resin cements were studied (Table 1). Each group of resin cement contained six subgroups (2 ceramic thicknesses x 2 different light curing times + 1 positive control (Direct light exposure; DLE) + 1 negative control (Self-

cured; SC)). Five specimens were prepared for each subgroup (n=5). The descriptions of the tested groups are given in Table 2.

TABLE 1. CONVENTIONAL AND SELF-ADHESIVE DUAL-CURE RESIN CEMENTS USED IN THIS STUDY

Resin cement	Manufacturer	Shade	Recommended light exposure protocol	Batch
Rely-X ARC	3M ESPE, St Paul, MN, USA	transparent	Light cure 40 sec / surface	N352609
Duolink	Bisco, Schaumburg, IL, USA	transparent	Light cure 40 sec / surface	1200003240
Rely-X U200 (Self adhesive)	3M ESPE, St Paul, MN, USA	transparent	Single surface, from occlusal : 20 sec Any other surface additional : 20 sec	491292
Maxcem Elite (Self adhesive)	Kerr, Orange, CA, USA	clear	Light cure 10 sec when irradiance is 1000 mW/cm² Light cure 20 sec when irradiance is 600 mW/cm²	4720553

TABLE 2. EXPERIMENTAL GROUPS WITH DIFFERENT CERAMIC THICKNESS AND CURING METHODS

Ceramic thickness (mm)	Curing time (sec)	Resin cements and code of experimental groups			
		Rely-X ARC	Duolink	Rely-X U200	Maxcem Elite
0	120	A DLE	D DLE	U DLE	M DLE
2	120	A 2-120	D 2-120	U 2-120	M 2-120
2	20	A 2-20	D 2-20	U 2-20	M 2-20
4	120	A 4-120	D 4-120	U 4-120	M 4-120
4	20	A 4-20	D 4-20	U 4-20	M 4-20
2	0	A SC	D SC	U SC	M SC

DLE: direct light exposure through the 2 mm-thick slide glasses; SC: Self-cure

3. MEASUREMENT OF THE CURING LIGHT INTENSITY

The power output (mW) of an LED curing light (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) was measured with a laser power meter (Powermax 5200, Molectron, Portland, OR, USA). The light transmittance value (mW/cm^2) through a ceramic block was calculated by dividing the

power output by the area of curing light tip. Measurements were repeated 5 times for each group and the average value was calculated (Table 3).

TABLE 3. LIGHT TRANSMITTANCE MEAN VALUES (SD) FOR EACH EXPERIMENTAL CONDITION (N=5)

Ceramic thickness (mm)	0 (Control)	2	4
Distance from light curing unit (mm)	2	2	4
Irradiance (mW/cm^2)	1085.4 (6.3) [a]	128.2 (2.6) [b]	25.6 (0.9) [c]

Significant differences are shown by different letters within row according to Student-Newman-Keuls post hoc test ($p<0.05$)

4. SPECIMEN PREPARATION

Resin cements were mixed according to the manufacturer's instructions and placed on a glass slide. Adhesive tape (Scotch tape, 3M, St. Paul, MN, USA) was applied to the glass slide before resin cement placement and served as a spacer (100±10μm) to ensure a constant thickness of the resin

cement layer. Then resin cement was covered with a mylar strip and pressed with another slide glass to remove the excess cement (Boaro et al., 2013; Martim et al., 2014; Salehi et al., 2015). Then a ceramic block (2 or 4 mm-thick) was placed above the mylar strip. For the SC group, a 2 mm-thick ceramic block was placed on the specimen. For the DLE group, additional slide glasses were placed over the specimen to control the distance between the light curing unit tip and the specimen at 2 mm. (Fig. 1).

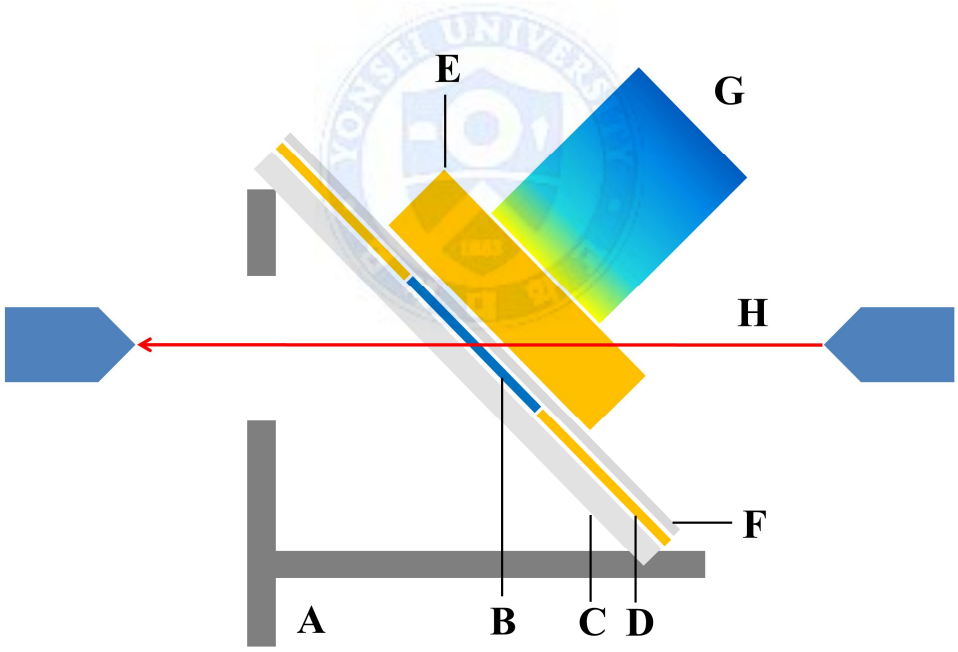

Figure 1. Specimen positioning

A: holder; B: resin cement; C: slide glass; D: spacer; E: ceramic block or slide glass; F: mylar strip; G: light curing unit tip; H: IR path

5. MEASUREMENT OF DEGREE OF CONVERSION

The specimen was mounted in a plastic holder and placed in the Fourier transform infrared spectrometer (Nicolet 6700 FT-IR Spectrometer, Thermo, Madison, WI, USA) at a 45° vertical angle. (Fig. 1) Infrared spectra were recorded immediately after the placement, and then the specimen was illuminated with the LED curing light (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) for 20 or 120 seconds, except for the self-cured group. Spectra collection was set up between 6140-6200 cm^{-1} on Transmission ESP, Near IR mode, taking 1 spectrum per second (2 scans/spectrum) at 4 cm^{-1} resolution. Data collection was continued for 600 seconds, and each test condition was replicated 5 times. Degree of conversion (DC) was calculated by the equation below. Polymerization rate curve was obtained by taking the first derivative of the DC with regard to time. The maximum value of the derivative was taken as the maximum polymerization rate (Rp max, DC %/sec), and the time required to reach the Rp max was taken as the time of maximum polymerization rate (Time of Rp max, sec).

DC (%) = [1- {Peak area (p) / Peak area (u)}] x 100 (%)

where “u” and “p” refer to the unpolymerized and polymerized cement, respectively, with the reaction peak set at 6165 cm^{-1} (Stansbury and Dickens, 2001; Yamasaki et al., 2013) ; Peak area (u) was calculated by averaging values over the first 20 seconds before light exposure (40 data points) and Peak area (p) was measured twice, at 10 minutes and 24 hours after data collection. Peak area (p) at 10 minutes was calculated by averaging values of the last 50 seconds (100 data points), and peak area (p) at 24 hours was calculated by averaging values for 20 seconds (40 data points) after 24 hours.

Polymerized specimens were removed from the holder after 10 minutes, and resin cement thickness was measured with a digital micrometer (Absolute Digimatic Caliper, Mitutoyo Corp., Aurora, IL, USA) to ensure uniform thickness among the specimens. Then specimens were stored in light-proof, dry conditions, at 25°C for 24 hours. Infrared spectrum was collected again for each specimen after 24 hours and the DC was calculated.

Infrared (IR) spectra data was extracted from the IR spectra analysis software package OMNIC 6.0 (Thermo Electron Inc., Madison, WI, USA). Raw data was analyzed by PeakFit v4.12 (Systat Software, Inc., San Jose, CA, USA) and smoothed under Loess algorithm, 2.0% level. A representative curve was obtained by averaging data of five specimens in each group.

6. STATISTICAL ANALYSIS

Statistical analysis was performed using SPSS version 20 (SPSS Inc., Chicago, IL, USA). For DC of resin cements, one-way analysis of variance (ANOVA) was done between 6 groups (4 experimental groups + 2 control groups) to compare DC(%) at 10 min, DC(%) at 24 h, maximum polymerization rate, and time of maximum polymerization rate, and Student-Newman-Keuls post hoc test was done for multiple comparisons. Then the paired t-test was done to compare DC(%) at 10 min, and DC(%) at 24 h for each group. For light transmission values of curing light, one-way ANOVA was done, followed with Student-Newman-Keuls post hoc test for multiple comparisons. ($\alpha = 0.05$)

III. Results

Table 4 shows the mean and standard deviations (SD) of the DC(%), maximum polymerization rate (DC %/sec), and time of maximum polymerization rate of the four resin cements. Light transmittance values for each experimental condition are given in Table 3.

TABLE 4. DC (%) (SD) AT 10 MINUTES AND 24 HOURS, RP MAX (DC %/SEC), AND TIME OF RP MAX (SEC)

	DC 10min	DC 24h	Rp max	Time of Rp max
A DLE	80.65 ^{Ab} (0.69)	86.97 ^{Aa} (0.97)	7.42 ^{A} (0.82)	4.55 ^{B} (0.73)
A 2-120	78.89 ^{Bb} (1.10)	86.48 ^{Aa} (0.97)	4.80 ^{B} (0.40)	7.33 ^{B} (1.23)
A 4-120	75.09 ^{Cb} (2.07)	85.29 ^{Aa} (2.27)	3.44 ^{C} (0.60)	13.07 ^{B} (1.97)
A 2-20	71.92 ^{Db} (1.02)	82.82 ^{Ba} (0.94)	4.73 ^{B} (0.38)	8.42 ^{B} (0.93)
A 4-20	63.46 ^{Eb} (1.71)	75.78 ^{Da} (2.22)	2.75 ^{D} (0.41)	10.69 ^{B} (2.23)
A SC	56.25 ^{Fb} (0.86)	78.98 ^{Ca} (1.68)	1.08 ^{E} (0.18)	137.38 ^{A} (33.14)

D DLE	69.27 ^{Ab} (1.66)	74.55 ^{Aa} (1.84)	7.51 ^{A} (1.22)	3.07 ^{B} (0.65)
D 2-120	69.62 ^{Ab} (1.44)	74.74 ^{Aa} (1.24)	3.98 ^{B} (0.61)	4.55 ^{B} (0.89)
D 4-120	69.69 ^{Ab} (1.20)	75.56 ^{Aa} (0.51)	2.47 ^{C} (0.22)	9.90 ^{B} (1.26)
D 2-20	62.95 ^{Bb} (1.30)	69.65 ^{BCa} (1.45)	4.17 ^{B} (0.36)	4.36 ^{B} (0.73)
D 4-20	60.23 ^{Cb} (1.13)	68.05 ^{Ca} (1.10)	2.52 ^{C} (0.27)	12.87 ^{B} (0.78)
D SC	53.79 ^{Db} (1.30)	70.91 ^{Ba} (1.23)	0.65 ^{D} (0.13)	144.10 ^{A} (42.04)
U DLE	65.38 ^{Ab} (1.21)	71.63 ^{Aa} (1.28)	5.04 ^{A} (0.90)	4.55 ^{B} (0.73)
U 2-120	65.47 ^{Ab} (1.70)	71.86 ^{Aa} (1.88)	2.80 ^{B} (0.29)	4.85 ^{B} (0.41)
U 4-120	63.75 ^{Ab} (1.27)	69.78 ^{Aa} (0.65)	2.59 ^{B} (0.45)	9.60 ^{B} (1.90)
U 2-20	56.92 ^{Bb} (1.53)	64.28 ^{Ba} (1.60)	3.00 ^{B} (0.36)	4.65 ^{B} (0.75)
U 4-20	49.39 ^{Cb} (2.44)	58.14 ^{Da} (1.69)	2.32 ^{B} (0.55)	7.03 ^{B} (2.85)
U SC	30.63 ^{Db} (2.81)	61.73 ^{Ca} (2.17)	0.61 ^{C} (0.27)	170.68 ^{A} (45.15)

M DLE	69.97 ^{Ab} (2.03)	75.48 ^{Aa} (2.18)	3.22 ^{A} (0.72)	4.36 ^{B} (1.07)
M 2-120	68.31 ^{Ab} (1.41)	74.56 ^{Aa} (1.69)	1.78 ^{B} (0.36)	7.33 ^{B} (1.54)
M 4-120	63.39 ^{Bb} (2.96)	70.80 ^{Ba} (3.49)	1.88 ^{B} (0.29)	10.89 ^{B} (1.64)
M 2-20	55.84 ^{Cb} (1.25)	64.57 ^{Ca} (1.07)	1.58 ^{B} (0.23)	7.72 ^{B} (1.34)
M 4-20	48.43 ^{Db} (3.11)	59.50 ^{Da} (2.33)	1.67 ^{B} (0.19)	10.79 ^{B} (1.33)
M SC	54.77 ^{Cb} (1.21)	69.61 ^{Ba} (1.14)	0.96 ^{C} (0.10)	94.50 ^{A} (14.83)

Significant differences are written by different letters (uppercase letters within column; lowercase letters between DC 10min and DC 24h) within each resin cement according to Student-Newman-Keuls post hoc test ($p<0.05$)

1. POLYMERIZATION KINETICS (0-10 MINUTES)

Figure 2 and 3 shows the effects of light curing condition on the real-time polymerization profiles for each resin cement. Generally, the dual-cure groups showed a rapid increase in DC immediately after the light exposure while the self-cure groups showed a more gradual increase.

Light curing time clearly influenced polymerization curves among dual-cure groups. When comparing the 2 mm-20 sec group against the 2 mm-120 sec group, the polymerization curves were similar up to 20-25 seconds after light exposure, but altered after that as a further increase in DC was observed in the group with continued light exposure up to 120 seconds. The same phenomenon was observed when comparing the 4 mm-20 sec and 4 mm-120 sec groups. (Fig. 3)

The maximum polymerization rate was 1.58-7.51%/sec in dual-cure groups and 0.61-1.08%/sec in self-cure groups (Table 4). The overlying ceramic thickness (0, 2, 4 mm-thick) significantly influenced Rp max and time of Rp max (Table 4), which is directly related to the polymerization profile before 20 seconds.

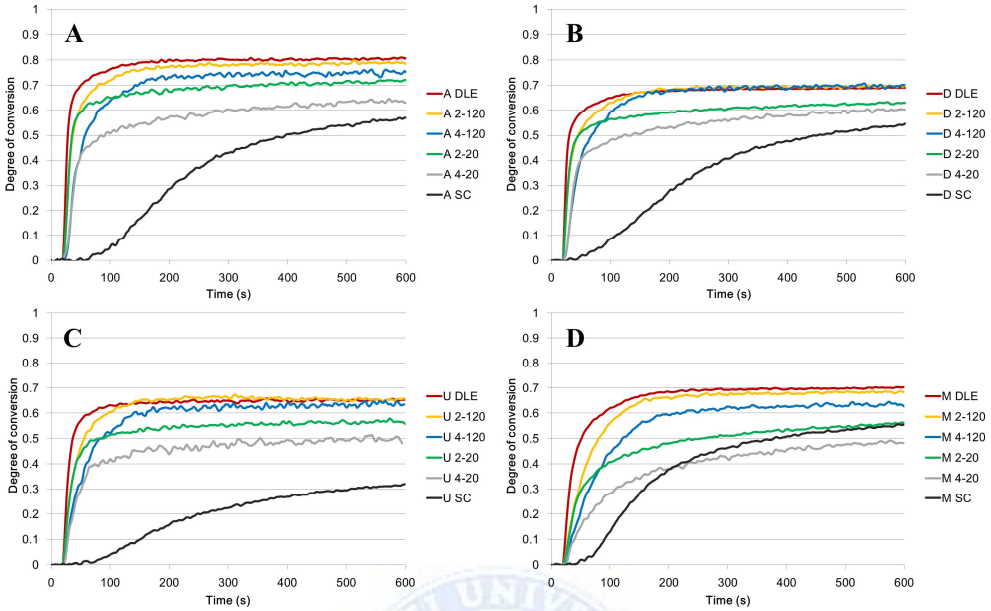

Figure 2. Representative real-time polymerization profiles of (A) Rely-X ARC, (B) Duolink, (C) Rely-X U200, (D) Maxcem Elite according to light curing condition during the initial 10 minutes.

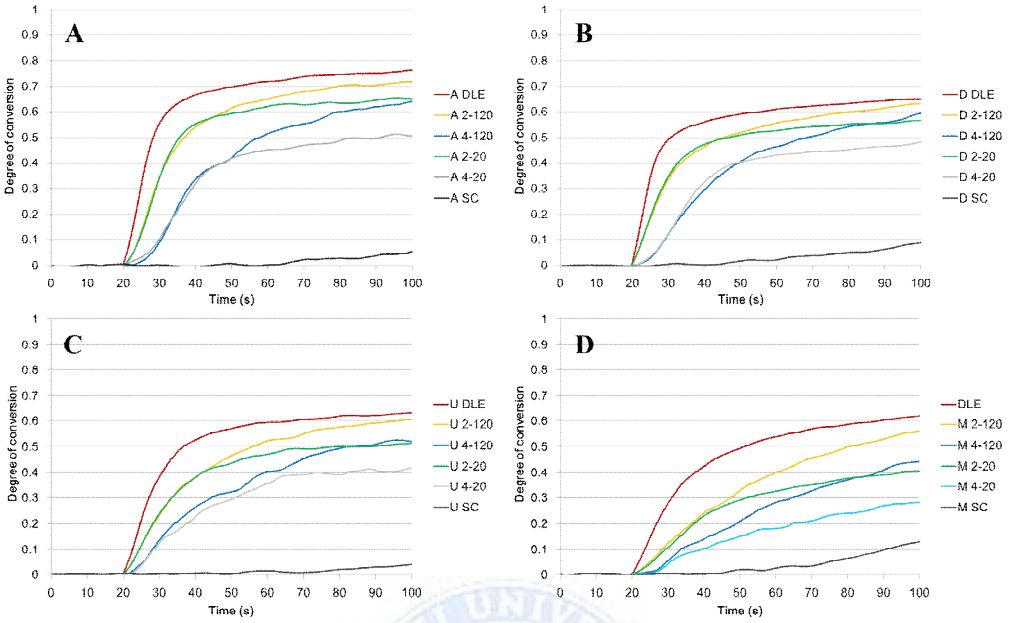

Figure 3. Representative real-time polymerization profiles of (A) Rely-X ARC, (B) Duolink, (C) Rely-X U200, (D) Maxcem Elite according to light curing condition during the initial 80 seconds.

2. DC (10 MINUTES AND 24 HOURS)

At 10 minutes after polymerization, significantly higher DC was observed in all dual-cure groups compared to the self-cure group, except Maxcem Elite at 2 mm-20 sec and 4 mm-20 sec. However, at 24 hours after polymerization, the DC of the self-cure groups equaled or surpassed that of the 4 mm-20 sec groups regardless of the material, and the M SC group showed

even higher DC compared with M 2-20 group ($p<0.05$), which means there was even more increase in the DC in the self-cure group between the two measurements. (Table 4)

The self-cured group revealed the highest DC increase for all resin cements when comparing 10 minutes and 24 hours (Table 4). For the dual-cured groups, the DC increase had a trend of inverse relationship with the amount of initial light energy received.

When light curing time was set to 20 seconds, the presence of the ceramic block significantly affected DC, resulting in significantly lower values at 24 hours after polymerization compared with the positive control group, which represents the maximum DC attainable ($p<0.05$). However when light curing time was set to 120 seconds, a similar DC compared to the positive control group ($p>0.05$) was achieved in all dual-cure groups at 24 hours, regardless of the ceramic thickness, except Maxcem Elite at 4 mm. (Table 4)

IV. Discussion

Based on the results of this experiment, the first hypothesis was rejected because the degree of conversion of all cements varied according to the curing conditions (Table 4). Especially all 4 mm-20 sec groups showed significantly lower DC compared to the SC groups at 24 hours after polymerization. This confirms that insufficient light exposure of a dual-cure resin cement could result in incomplete polymerization, resulting in a DC that is even lower than if the cement had been allowed to undergo self-curing alone. This is consistent with previous studies (Meng et al., 2008; Oliveira et al., 2012).

As dimethacrylate-based dental composites are polymerized, mobility of radicals become restricted by the growing cross-linked polymer network, and radicals become essentially immobilized after the vitrification point (Leprince et al., 2013). In the dual-cure mode, light-activation induces rapid polymerization, with large amounts of free radicals becoming trapped within the organic matrix at the initial stage of polymerization if insufficient curing energy is applied to drive the reaction further to completion (Leprince et al., 2010; Leprince et al., 2013; Truffier-Boutry et al., 2006). Considering that the self-cure mechanism proceeds more slowly, the rapid vitrification brought on

by the initial light activation necessarily minimizes the extent of the subsequent self-polymerization of the dual-cure resin cement, due to severe limitations in molecular mobility (Meng et al., 2008).

When a sufficient amount of light energy is delivered to a dual-cure resin cement, this kind of competitive reaction would not be apparent because the dual-cure resin cement has been polymerized well even if the self-cure component becomes partially impaired. In contrast, in the absence of light energy being delivered to the resin cement, a certain degree of polymerization is still attained solely due to the progress of the self-cure component. Therefore, if insufficient energy can be applied to the cement, it would be better, from the standpoint of DC, to simply allow the self-cure reaction to progress without light exposure.

However, regarding clinical application, it should be considered that the self-cure reaction progresses more slowly than the dual-cure reaction. In this study, DC of self-cured groups ranged 46.9-78.3% level of the positive control group at 10 minutes after polymerization (69.75% for Rely-X ARC, 77.65% for Duolink, 46.85% for Rely-X Unicem, 78.28% for Maxcem Elite), whereas previous studies assumed the polymerization level which provides clinically acceptable mechanical properties for resin composite as 80% level of the positive control (Moraes et al., 2012; Yamasaki et al., 2013). Therefore,

it appears that at least 10 minutes of polymerization time would be required for resin cements used in this study when they are applied in self-cure mode.

The second hypothesis was also rejected, because when the curing time was short (20 sec), the DC of all cements under 4 mm thickness of ceramic was lower than that achieved under a 2 mm thick ceramic. However this deficit could be overcome by increasing curing time, except for Maxcem Elite. When the other conditions were the same, the increased curing time increased DC of the cements in all of the experimental groups. Thus the third hypothesis also was rejected.

The interposition of a ceramic restoration exponentially decreases light transmission as the ceramic thickness increases (Kilinc et al., 2011; Lee et al., 2008; Meng et al., 2006; Moraes et al., 2008). Similar light attenuation was observed in this study, to about 1/40 of the level (25.6 mW/cm^2) of its original intensity (1085.4 mW/cm^2) as the ceramic thickness increased to 4 mm. Nevertheless, this low irradiance was still sufficient to induce significant curing of the resin composite (Musanje and Darvell, 2003), which in turn caused the severe impairment of the self-curing of the 4 mm-20 sec groups in this study.

This study also found that the dual-cured groups revealed different degrees of delayed polymerization according to the light curing condition.

This is explained by assuming that different initial polymer networks were developed for each dual-cured group depending on the light energy received during photo-curing, thus producing different barriers to the diffusion of chemical initiators after the light exposure. It has already been reported that delayed polymerization could be inhibited by the initial polymer network generated by light-activation (Meng et al., 2008), which explains the 1.3-5 times more delayed polymerization of the self-cured group compared to the dual-cured groups in this study. However, this finding also implies that the amount of delayed polymerization could depend on the complexity of the initial polymer network formed, even in the dual-cured groups.

When considering that the total light energy applied for the DLE group (130,248 mJ/cm^2) was about 40 times higher compared to the 4 mm-120 sec group (3,072 mJ/cm^2) in this study, the similar DC of both groups cannot be explained based on the light energy-based polymerization concept. However, recent studies suggest that DC is not directly proportional to the total amount of energy applied to resin cement (Feng and Suh, 2007; Feng et al., 2009; Musanje and Darvell, 2003). It should be noted that the light energy (mJ/cm^2) reveals simply the number of photons per unit area, and delivering more photons does not necessarily result in more activated photo-initiators and free radicals, because of rapid saturation of the photo-initiator system and

restricted availability of monomers (Feng and Suh, 2007; Feng et al., 2009). Therefore, the large discrepancy of received light energy between the two groups cannot be the key factor explaining the polymerization of the 4 mm-120 sec group. Musanje et al. (Musanje and Darvell, 2003) reported that when sufficiently long light curing time is provided, adequate polymerization can be achieved even at very low light irradiance (25 mW/cm^2). Although 'sufficiently long' light curing time would vary depending on the composition of the resin cement, 120 seconds of light curing time was effective on three out of the four resin cements tested in this study. Therefore prolonged light curing time could be an option to improve the polymerization level of dual-cure resin cement, depending on the specific composition of each resin cement. The exact length of the prolonged curing time would need to be determined for each specific cement.

Rely-X U200 showed low DC in self-cure mode at 10 minutes after mixing, being less than half of that of U DLE group. However, it should be noted that the DC recovered to a level similar to that of U 2-20 ($p>0.05$), showing a large amount of delayed polymerization (Table 4). Such low initial polymerization rate and large delayed polymerization is a general feature of self-adhesive dual-cure resin cements, and others have pointed out the presence of acidic functional monomers in the self-adhesive dual-cure resin

cements as one of the causes (Ferracane et al., 2011; Moraes et al., 2011). Acidic functional monomers have been suggested to deactivate free radicals of methacrylate and produce an acid-base setting reaction, inducing a low rate of co-polymerization and increased delayed polymerization (Ferracane et al., 2011). As shown in this study, self-adhesive dual-cure resin cements experienced large delayed polymerization which continued up to 24 hours, and probably 7 days according to recent studies (Baena et al., 2012). Therefore, it needs sufficient time to properly evaluate the polymerization of self-adhesive dual-cure resin cements. Also, the self-curing potential of self-adhesive dual-cure resin cements might be understated if it is evaluated at 10-30 minutes after polymerization, as reported in previous studies (Aguiar et al., 2010; Arrais et al., 2014; Moraes et al., 2011).

On the contrary, Maxcem Elite showed high RP max in the self-cure mode, which was resulted in higher DC compared with M 4-20 group at 10 minutes, and DC even higher than the M 2-20 group at 24 hours after polymerization ($p<0.05$) (Table 4). This high self-curing potential of Maxcem Elite has already been described in previous studies, and higher amounts of self-curing components than other self-adhesive dual-cure resin cements and use of amine-free redox initiator system were suggested as the possible explanation (Arrais et al., 2014; Moraes et al., 2011). Although a definitive

explanation has not been given due to a lack of information from the manufacturers, such high self-curing potential of Maxcem Elite seems to be suitable to obtain rapid polymerization in cases with gold or zircornia crowns, where there is little chance for light-activation of the cement.

An attenuated total reflectance (ATR) accessory has been used with a Fourier transform infrared spectrometer in most studies on the polymerization kinetics of resin composite (Aguiar et al., 2010; Archegas et al., 2012; Arrais et al., 2008; Arrais et al., 2009; Frassetto et al., 2012; Moraes et al., 2008; Moraes et al., 2011; Oliveira et al., 2012; Passos et al., 2013; Tezvergil-Mutluay et al., 2007; Yan et al., 2010). However, only the bottom layer of the resin specimen (about 1-2 μm) can be analyzed in the ATR setting. When considering that the polymerization level can vary depending on the location within a layer of dual-cure resin cement (Puppin-Rontani et al., 2012), ATR may not be the best method to assess the overall quality of the resin cement layer. Therefore in this study, the infrared beam path was designed to penetrate the full-thickness of the resin cements. For this purpose, near-IR, with greater penetration was selected instead of mid-IR, and the specimen was mounted on a holder at a 45° vertical angle in order to avoid blockage of the IR path by the light curing tip (Fig. 1). In this method, the IR beam penetrates the overlying ceramic block as well as the resin cement layer. However it is well known that

ceramic does not alter the infrared spectrum, although it does reduce the intensity (Fuller et al., 1968), and we could not find any disturbance of the IR spectrum by the ceramic interposition compared with the background spectrum.

V. Conclusion

Within the limitations of this study, the following conclusions could be made: When a ceramic restoration thickness is 4 mm or greater, 20 seconds of light curing time could result in a poor extent of polymerization, even lower than that of self-curing alone. Prolonging light curing time (120 seconds) could be an option to improve polymerization of conventional and self-adhesive dual-cure resin cements.

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국문요약

광조사 시간 및 세라믹 수복물의 두께가 통상 및 자가-접착형 이원-중합 레진 시멘트의 중합에 미치는 영향

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장 영 준

본 연구는 세라믹 수복물 하에서 광조사 시간이 이원-중합 레진 시멘트의 중합에 미치는 영향을 조사하는 것을 목적으로 하였다.

총 4종류의 이원-중합 시멘트가 서로 다른 광조사 조건 (이원-중합 또는 자가-중합), 광조사 시간 (20초 또는 120초), 다른 두께 (2 mm 또는 4 mm) 의 세라믹 수복물 하방에서 중합되었다. 초기 10분 동안, 그리고 24시간 후의 중합률이 FTIR 에 의해 실시간으로 측정되었다. 측정값들은 One-way ANOVA, Student-Newman-Keuls 사후 검정, 그리고 paired t-test 에 의해 통계 처리되었다.

광조사 시간이 20초일 경우, 세라믹 수복물은 중합률에 유의한 영향을 미쳤다. 특히 중합 시작 후 24시간이 경과하였을 때 4 mm-20 sec

군들은 자가-중합된 군들보다도 유의하게 낮은 중합률을 보였다. ($p<0.05$) 반면에 광조사 시간이 120초일 경우 Maxcem Elite 를 제외한 모든 이원-중합된 군들은 양성 대조군과 유의한 차이가 없는 양호한 중합률을 보였다.

결론적으로, 세라믹 수복물의 두께가 4 mm 이상일 경우 20초의 광조사 시간은 자가-중합 시보다도 더 낮은 중합률을 초래할 수 있는 위험이 있다. 한편 광조사 시간을 120초로 증가시키는 것은 세라믹 수복물 하에서 이원-중합 시멘트의 중합률을 높일 수 있는 방법 중 하나인 것으로 보인다.

핵심되는 말 : 세라믹, 광조사 시간, 중합률, 중합 동역학, 레진 시멘트